

**CHEMICAL ACTIVITIES OF ALKALI SULFATES  
IN HOT CORROSION**

**by**

**Chen C. Hsu, Irving Johnson,  
and Milton Blander**



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**ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS**

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ARGONNE NATIONAL LABORATORY  
9700 South Cass Avenue  
Argonne, Illinois 60439

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Chemical Engineering Division

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# CHEMICAL ACTIVITIES OF ALKALI SULFATES IN HOT CORROSION

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## ABSTRACT

The condensation temperatures of sodium and potassium sulfates from typical fuel-oil combustion gases were calculated as functions of the concentrations of  $\text{SO}_2$ ,  $\text{HCl}$ ,  $\text{NaCl}$  and  $\text{O}_2$ , and total combustion pressures ranging from 1 to 10 atm. Of these components, oxygen had the greatest effect on the condensation temperature of sodium sulfate, producing an increase of as much as 280 K at 10 atm. Alkali sulfate activities were least affected by sulfur dioxide, tested in the range from 93 to 270 ppm. The order of the effect on the alkali sulfates was as follows:  $\text{O}_2 > \text{HCl} > \text{NaCl} > \text{SO}_2$ . With the addition of  $\text{K}_2\text{CO}_3$ , such as would occur in the magnetohydrodynamic (MHD) environment, the activity of potassium sulfate overshadowed that of sodium sulfate. The control of the activities of alkali sulfates is discussed in terms of the concentrations of the above-mentioned species and of the system pressure.

## I. INTRODUCTION

One of the means of increasing the overall efficiency of the operation of a gas turbine is to increase the turbine inlet temperature. However, the increase of the turbine temperature is limited by the high-temperature strength of the superalloys which are used as turbine construction materials. With the reduction of chromium content from 20 to 10% in superalloys, the gas turbine suffers serious corrosion problems. Hot corrosion, that is accelerated oxidation, is most often attributed to the presence of trace impurities of sodium chloride and sulfur in the fuels. In the case of marine gas turbines, sodium chloride comes mainly from an aerosol of seawater. For other turbine uses, the result of corrosion analysis reveals that liquid  $\text{Na}_2\text{SO}_4$  is the species responsible for hot corrosion.<sup>1-2</sup> Experiments<sup>3-10</sup> have been carried out in various laboratories to elucidate the mechanism of hot corrosion of superalloys. As a result of these investigations, Goebel and Pettit<sup>10</sup> proposed three possible mechanisms as being involved in hot corrosion, namely, basic and acidic fluxing reactions, and sulfidation. The destruction of the protective oxide layer on the metal surface followed by depletion of the newly exposed metal by reaction with oxide ions in a  $\text{Na}_2\text{SO}_4$  melt is called the basic fluxing reaction, while a similar reaction is called an acidic fluxing reaction if the oxide ion is donated by the oxide barrier. The formation of sulfides by reaction of the metal oxides with  $\text{Na}_2\text{SO}_4$  gives rise to an accelerated oxidation called sulfidation. Regardless of the mechanism involved, a sufficient condition leading to catastrophic oxidation is the presence of liquid alkali sulfates in the oxidizing environment in the high-temperature combustion system. An understanding of the conditions that result in the

formation of alkali sulfates in the combustion systems becomes important to the control of hot corrosion. This is even more important in the magnetohydrodynamic (MHD) environment where a potassium salt is artificially injected as seed into the generator channel. In this report, the condensation temperatures of potassium and sodium sulfates and a thermodynamic analysis of the important species in the combustion systems are presented. In addition, optimum operational conditions for gas turbines are suggested.

## II. CALCULATIONS

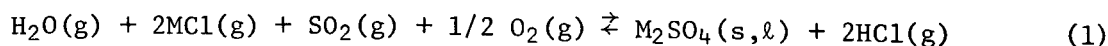
The stable species present in a system at equilibrium were determined by means of the NASA code<sup>11</sup> for calculation of equilibrium compositions (CEC) and an ANL modification of the CEC code,<sup>12</sup> both of which utilize the technique of minimization of the free energy of the system. The typical composition of a fuel-oil combustion gas used for these calculations is given in Table 1.

Table 1. Typical Composition of a Fuel-Oil Combustion Gas.

Constituent	Concentration <sup>a</sup>
O <sub>2</sub>	9.59 mol %
N <sub>2</sub>	76.21 mol %
CO <sub>2</sub>	8.57 mol %
H <sub>2</sub> O	5.63 mol %
SO <sub>2</sub>	185 ppm
HCl	40 ppm
NaCl	10 ppm
KCl	7 ppm

<sup>a</sup> 1 ppm = 10<sup>-4</sup> mol %.

The formation of the alkali sulfates as condensed phases can occur according to the reaction:



where M is either potassium or sodium. (Other equilibria involved in the combustion will not be discussed here.) The activities of the alkali sulfates were calculated as functions of the concentrations of NaCl, SO<sub>2</sub>, HCl, O<sub>2</sub>; the temperature; and the system pressure. The pressure ranged from 1 to 10 atm and the temperature from 900 to 1500 K. The effect on the equilibrium of adding small amount of K<sub>2</sub>CO<sub>3</sub> was also studied. Unless otherwise noted, the



criterion for determining whether a species was present at a significant level in the equilibrium mixture was set at  $5 \times 10^{-6}$  mol % (50 ppb). The composition of the combustion gas given in Table 1, which served as the baseline case, was varied in separate calculations as follows:

- (1) NaCl: 10 ppm, 1 ppm, 100 ppb, and 10 ppb
- (2) SO<sub>2</sub>: 92.5, 185, and 270 ppm; NaCl: 10 and 1 ppm
- (3) HCl: 4, 40, and 400 ppm; NaCl: 10 and 1 ppm
- (4) O<sub>2</sub>: 10, 1, and 0 ppm
- (5) O<sub>2</sub>: 0; CO: 42.9 ppm
- (6) K<sub>2</sub>CO<sub>3</sub>: 1, 10, 100, and 1000 ppm

The computer output comprised a listing of stable species and their corresponding mole fractions at equilibrium under the specified values of the temperature and pressure. The partial pressure of each species was obtained simply by multiplying the mole fraction by the system pressure.

### III. THERMODYNAMIC EQUILIBRIUM

The equilibrium compositions and the condensation temperatures of the alkali sulfates are affected by the concentration of NaCl, SO<sub>2</sub>, O<sub>2</sub>, and K<sub>2</sub>CO<sub>3</sub>, in the input as well as by the system pressure. Figure 1 shows the gas phase equilibrium for a system at equilibrium with the initial gas having the typical composition listed above. At the higher temperature end, the equilibrium composition consists of NaCl, HCl and SO<sub>2</sub>. Notice the sharp increase of Na<sub>2</sub>SO<sub>4</sub> as the temperature is lowered. At 1192 K, Na<sub>2</sub>SO<sub>4</sub> starts to condense and a drastic decrease in the concentrations of NaCl and Na<sub>2</sub>SO<sub>4</sub> occurs in the gas phase. The concentration of HCl increases, as expected from Eq. 1, as more of the Na<sub>2</sub>SO<sub>4</sub> condenses. At the lower temperature, the equilibrium gas contains only SO<sub>2</sub> and HCl. With the addition of 100 ppm of K<sub>2</sub>CO<sub>3</sub> to the initial gas, the amount that would be expected in a MHD system, the equilibrium composition on the high-temperature side is gaseous K<sub>2</sub>SO<sub>4</sub>, NaCl, and HCl; and on the low-temperature side, it is SO<sub>2</sub> and HCl, as shown in Fig. 2. The sharp decrease in the partial pressure of gaseous K<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> begins at 1310 K, the temperature at which K<sub>2</sub>SO<sub>4</sub> starts condensing. The decrease of NaCl concentration takes place at 1215 K when Na<sub>2</sub>SO<sub>4</sub> begins to condense. The condensation temperature of Na<sub>2</sub>SO<sub>4</sub> increases about 20 K with the addition of 100 ppm K<sub>2</sub>CO<sub>3</sub> to the input gas. Comparison of Figs. 1 and 2 shows that the HCl partial pressure is lowered from  $4 \times 10^{-5}$  atm at 1100 K to  $10^{-6}$  atm at 1500 K by the addition of the K<sub>2</sub>CO<sub>3</sub>. A sharp increase in HCl partial pressure takes place after K<sub>2</sub>SO<sub>4</sub> condensation begins. The effects of each gas constituent on the formation of alkali sulfates are discussed individually below.

#### A. The Effect of NaCl

In general, lowering the concentration of NaCl decreases the condensation temperature of Na<sub>2</sub>SO<sub>4</sub>. The condensation temperature of Na<sub>2</sub>SO<sub>4</sub> is decreased by 88 and 108 K at 1 and 10 atm, respectively, when the NaCl is lowered from 10 to 1 ppm. The calculations also were carried out for 100 and 10 ppb of NaCl. Although the NaCl level is again decreased by a factor of ten, the effect on the Na<sub>2</sub>SO<sub>4</sub> condensation temperature is less at the lower NaCl levels. Lowering the NaCl level from 100 to 10 ppb results in a decrease of about 60 K

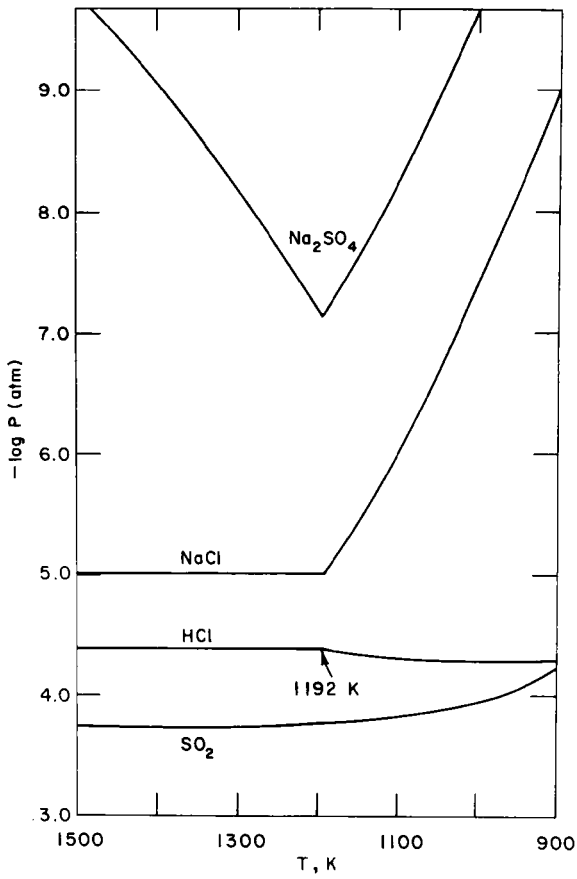
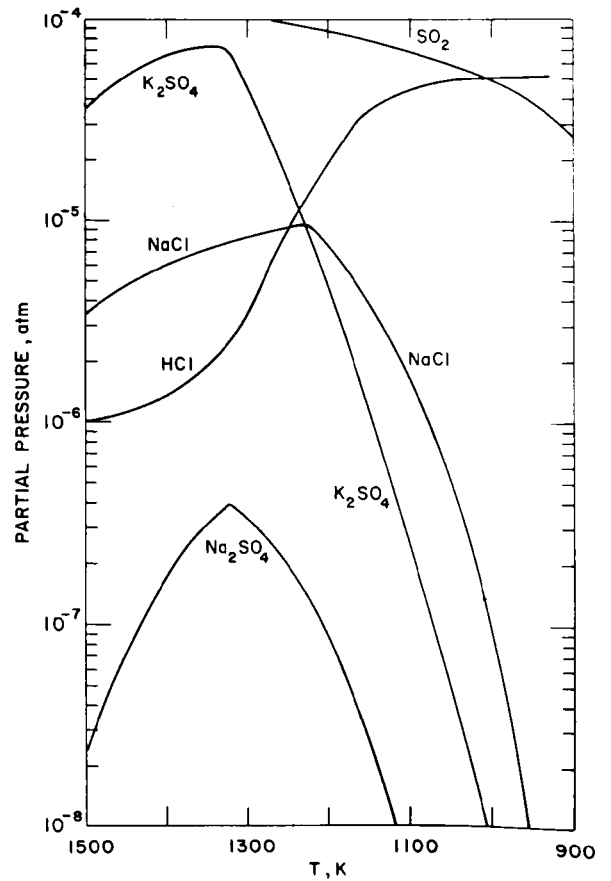


Fig. 1.

Gas Phase Equilibrium of Combustion Gas.

Fig. 2.

Gas Phase Equilibrium of Combustion Gas Doped with 100 ppm  $\text{K}_2\text{CO}_3$ .



at 1 atm and 78 K at 10 atm. The results are shown in Fig. 3. Changing the system pressure from 1 to 10 atm increases the  $\text{Na}_2\text{SO}_4$  condensation temperature by about 20 K for all four NaCl concentrations. These results are consistent with those of Westinghouse.<sup>13</sup> In the presence of a higher HCl concentration (400 ppm as compared with 40 ppm), the condensation temperature of  $\text{Na}_2\text{SO}_4$  decreases from 1192 to 1106 K at 1 atm and from 1321 to 1213 K at 10 atm with 10 ppm NaCl present; and from 1115 to 1025 K at 1 atm and from 1211 to 1115 K at 10 atm with 1 ppm NaCl present, as shown in Fig. 4.

The concentration of NaCl has little effect on the condensation temperature of  $\text{K}_2\text{SO}_4$ . When the NaCl level is lowered from 10 ppm to 1 ppm, the condensation temperature of  $\text{K}_2\text{SO}_4$  increases only 10 K at both 1 and 10 atm, as shown in Fig. 5. With further decreases in NaCl concentration levels to 100 ppb and 10 ppb, the  $\text{K}_2\text{SO}_4$  condensation temperature is not different from the value observed at 1 ppm NaCl. Because the melting point of  $\text{K}_2\text{SO}_4$  is higher than that of  $\text{Na}_2\text{SO}_4$  (1342 vs. 1157 K), it is less important as a corrodant in combustion systems unless it condenses with  $\text{Na}_2\text{SO}_4$ .

#### B. The Effect of $\text{SO}_2$

The change in the condensation temperature of  $\text{Na}_2\text{SO}_4$  due to the variation of the  $\text{SO}_2$  concentration is shown in Fig. 6. The increase in the condensation temperature of  $\text{Na}_2\text{SO}_4$  owing to a doubling of the concentration of  $\text{SO}_2$  (185 ppm as base concentration) with 1 ppm NaCl present is only 5 K at 1 atm and 15 K at 10 atm. With half of the base  $\text{SO}_2$  concentration, the condensation temperature decreases 15 K at 1 atm and 20 K at 10 atm. With 10 ppm of NaCl present, the temperature changes are almost identical to those with 1 ppm NaCl except that the  $\text{Na}_2\text{SO}_4$  condensation temperature undergoes a shift to higher temperatures; this shift is 75 K at 1 atm and 110 K at 10 atm. In the case of  $\text{K}_2\text{SO}_4$ , the condensation temperature is fairly insensitive to the increase and decrease in concentrations of  $\text{SO}_2$  and NaCl (see Fig. 7). This is to be expected because the activity of  $\text{SO}_2$  remains very high at equilibrium in the temperature range of interest, Fig. 1. The former case has been verified experimentally by Hanby,<sup>14</sup> who found that there is no significant effect on the sulfation rate of NaCl when the sulfur content of the fuel is reduced from 1 to 0.1 wt % (thus reducing the  $\text{SO}_2$  content of the combustion gas also).

#### C. The Effect of HCl

An increase in HCl concentration causes the condensation temperature of  $\text{Na}_2\text{SO}_4$  to decrease considerably. Figure 4 shows the results of three different HCl concentrations, 4, 40, 400 ppm with two NaCl concentrations, 10, and 1 ppm. The decrease in the  $\text{Na}_2\text{SO}_4$  condensation temperature with 1 ppm NaCl present is about 90 K at both 1 and 10 atm when the HCl concentration is increased from 40 to 400 ppm. It is about the same for the increase from 4 to 40 ppm HCl, except at lower pressures, where the decrease is 75 K. These results apply to the case with 10 ppm NaCl present, except that the condensation temperature of the  $\text{Na}_2\text{SO}_4$  is systematically shifted 80 K higher for all concentrations of HCl. This trend is expected since an increase in NaCl concentration gives rise to an increase in sodium ion concentration and this in turn leads to an increase in the concentration of  $\text{Na}_2\text{SO}_4$ . In the case of  $\text{K}_2\text{SO}_4$ , the increase in HCl concentration from 40 to 400 ppm with 10 ppm NaCl present causes a decrease in the condensation temperature of  $\text{K}_2\text{SO}_4$  (see Fig. 8). It should be noted that at

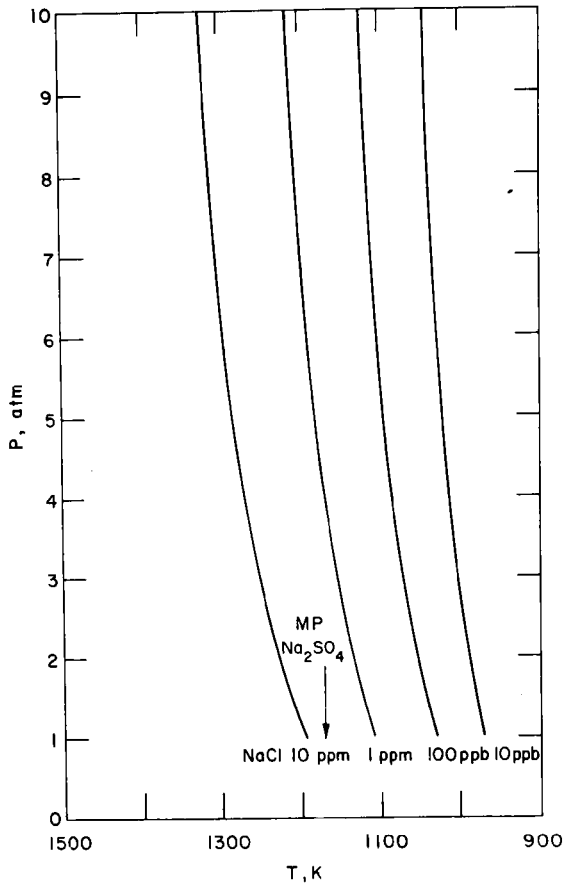
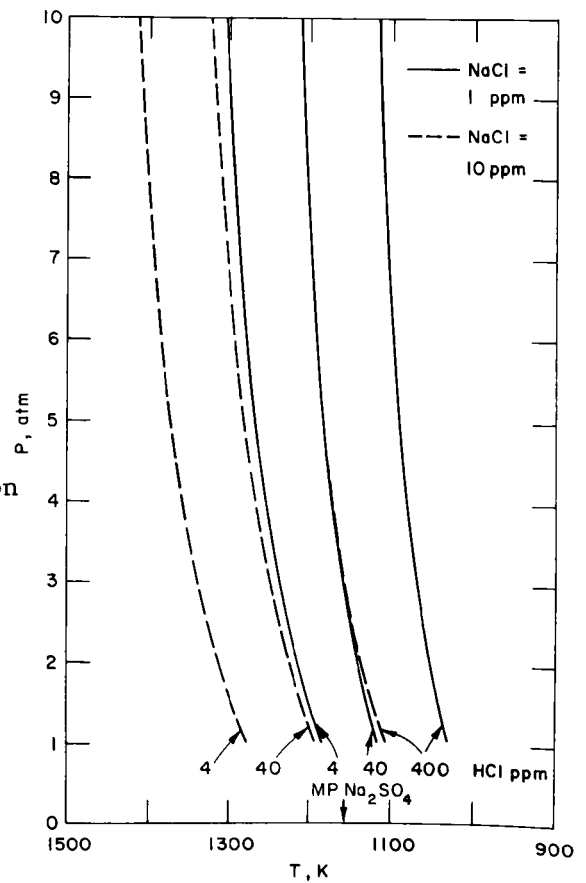


Fig. 3.

Condensation Temperature of  $\text{Na}_2\text{SO}_4$  as a Function of Pressure and NaCl Concentration.

Fig. 4.

Condensation Temperature of  $\text{Na}_2\text{SO}_4$  as a Function of Pressure and Concentration of HCl and NaCl.



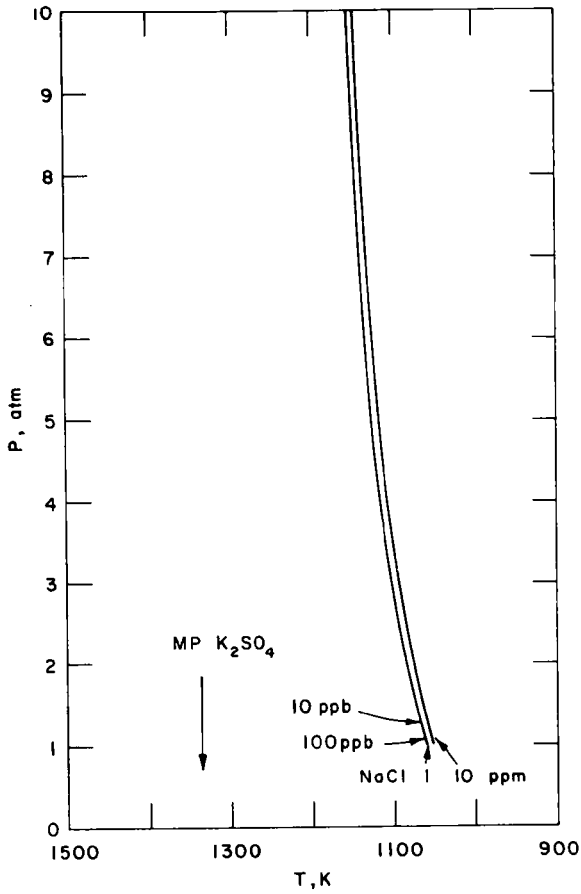
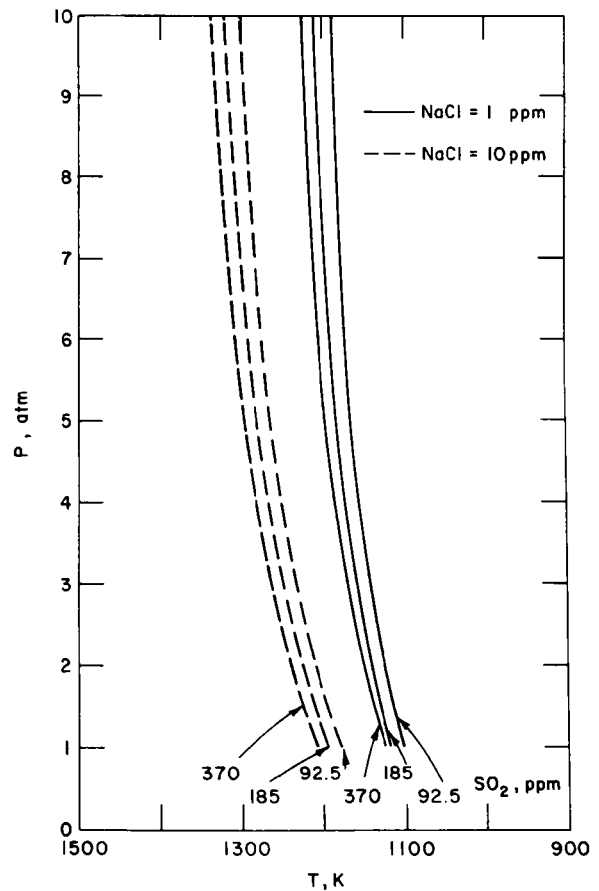


Fig. 5.

Condensation Temperature of  $K_2SO_4$  as a Function of Pressure and NaCl Concentration.

Fig. 6.

Condensation Temperature of  $Na_2SO_4$  as a Function of Pressure and Concentrations of  $SO_2$  and NaCl.



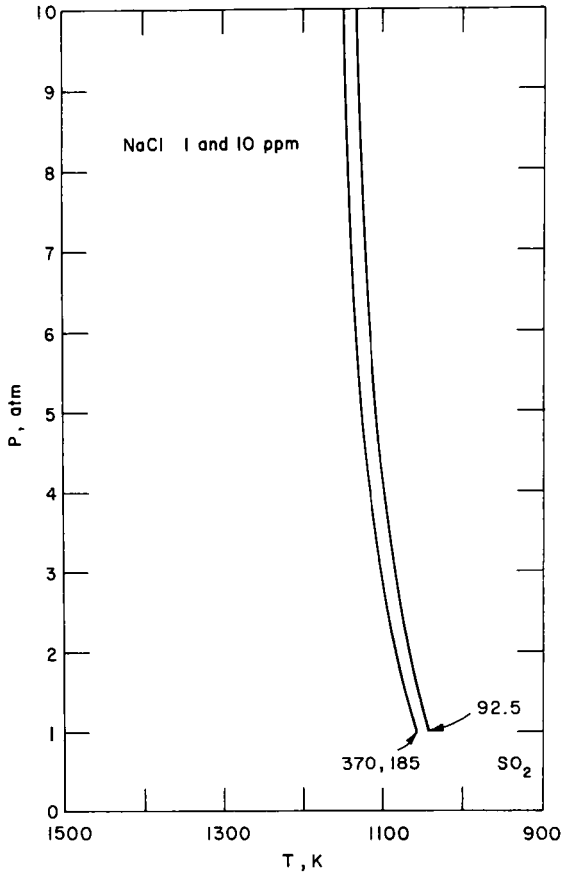
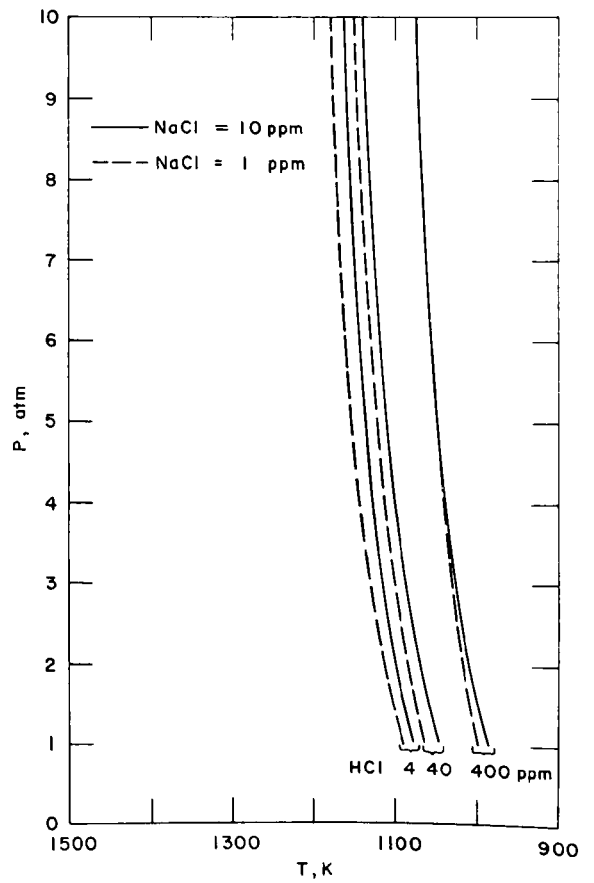


Fig. 7.

Condensation Temperature of  $K_2SO_4$  as a Function of Pressure and NaCl Concentration.

Fig. 8.

Condensation Temperature of  $K_2SO_4$  as a Function of Pressure and Concentrations of HCl and NaCl.



400 ppm HCl, the condensation temperature of  $K_2SO_4$  is almost identical for both 1 ppm and 10 ppm NaCl, thereby indicating that, at this level of HCl concentration, the  $K_2SO_4$  condensation temperature is independent of NaCl concentration.

#### D. The Effect of $O_2$

In order to understand the effect of oxygen on the formation of  $Na_2SO_4$ , the calculation was first carried out without free oxygen in the input combustion gas. The results are shown in Fig. 9. With 10 ppm NaCl present, the decrease in the  $Na_2SO_4$  condensation temperature is 125 K at 1 atm and 148 K at 10 atm, whereas with 1 ppm NaCl, the decrease is 220 K at 1 atm and 235 K at 10 atm. This clearly suggests that the formation of condensed  $Na_2SO_4$  depends very strongly on oxygen activity. The calculation was carried out further by replacing the free oxygen in the input gas with 42.9 ppm of CO in the presence of 10 ppm NaCl. The condensation temperature of  $Na_2SO_4$  decreased by 250 K at 1 atm and by 280 K at 10 atm. These results imply that under certain reducing conditions in the turbine, condensation of  $Na_2SO_4$  can be avoided. For  $K_2SO_4$ , the effect of no free oxygen is not as great as it was for  $Na_2SO_4$ , as can be shown from the results of condensation temperature calculations with the typical composition of a combustion gas, except that the NaCl was 1 ppm (see Fig. 9). With 1 ppm NaCl, the reduction in the  $K_2SO_4$  condensation temperature is 134 K at 1 atm and 160 K at 10 atm. If the operational temperature remains higher than 930 K, the condensation of  $K_2SO_4$  would not take place. This result is in consonance with the consideration of operating an MHD combustor under slightly reducing conditions to prevent the condensation of alkali sulfates, especially  $K_2SO_4$ .

#### E. The Effect of the Addition of Trace $K_2CO_3$

In the MHD environment, the potassium concentration is much higher than that of sodium since potassium salts are injected into the MHD generator as seed to create a high plasma density with high velocity. The equilibrium compositions of the combustion gas were altered drastically as a result of doping with a trace amount of  $K_2CO_3$ , as may be seen by comparing Figs. 1 and 2. Consequently, the condensation temperature of  $Na_2SO_4$ , as well as that of  $K_2SO_4$ , is affected to a great extent. For  $Na_2SO_4$ , the condensation temperature is decreased from 1192 to 936 K with 1000 ppm of  $K_2CO_3$ , (Fig. 10). This is a reversal of the trend of increasing condensation temperature for concentrations of  $K_2CO_3$  that are less than 100 ppm, although the increase is not significant (about 15 K). No change in the condensation temperature of  $Na_2SO_4$  occurred with the addition of 1 ppm  $K_2CO_3$ . In the case of  $K_2SO_4$ , the increase in the condensation temperature is considerable: 35, 125, 275, and 320 K with additions of 1, 10, 100, and 1000 ppm  $K_2CO_3$ , respectively, at 1 atm; and 45, 135, and 315 K with additions of 1, 10, and 100 ppm  $K_2CO_3$ , respectively, at 10 atm. To prevent the hot corrosion problems due to liquid  $K_2SO_4$  in the temperature range from 1500 to 900 K, the amount of  $K_2CO_3$  must be kept below 100 ppm, a concentration below which  $K_2SO_4$  condenses as a solid without going through the liquid-to-solid transformation.

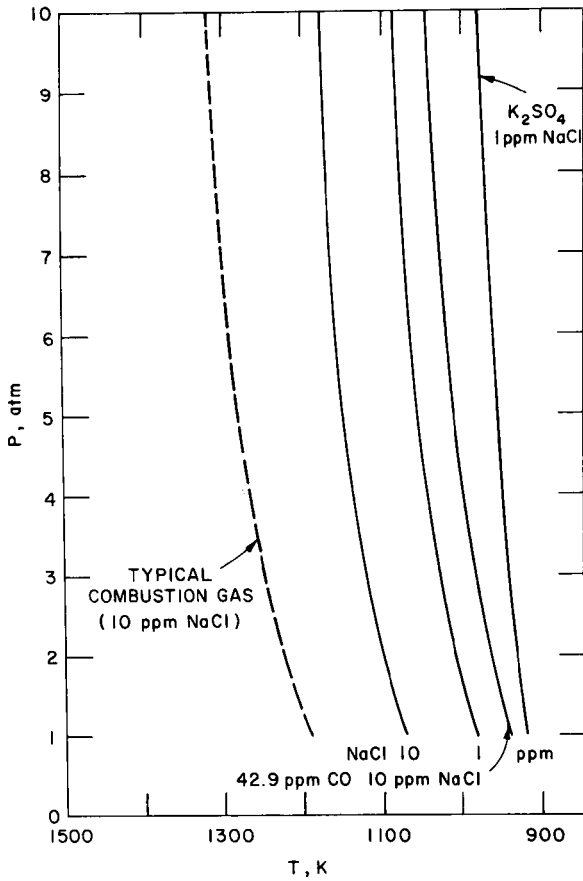
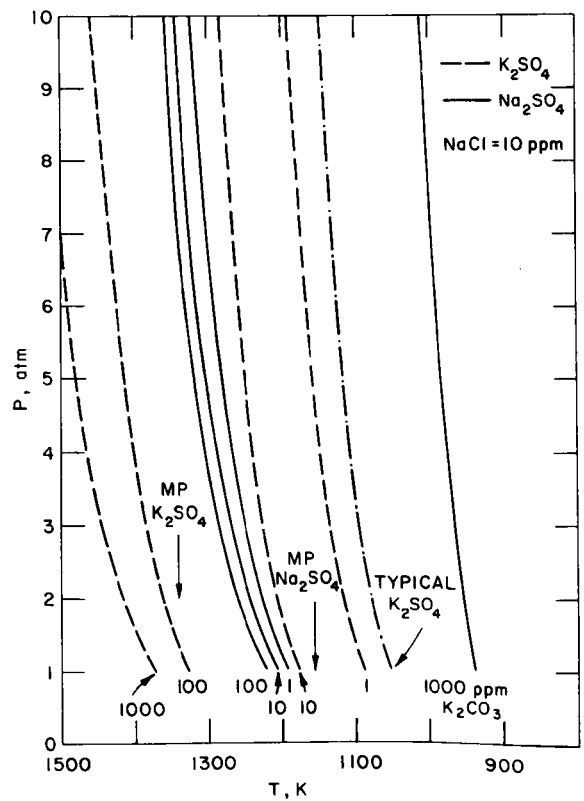


Fig. 9.

Condensation Temperature of  $\text{Na}_2\text{SO}_4$  as a Function of NaCl in the Absence of  $\text{O}_2$ .

Fig. 10.

Condensation Temperatures of  $\text{K}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$  as a Function of Pressure and  $\text{K}_2\text{CO}_3$  Concentration.





## IV. DISCUSSION

The results obtained above are based on a thermodynamic equilibrium model. Although the residence time in the combustion chamber might be too short to allow equilibrium to be achieved, the instantaneous concentration of alkali sulfates can greatly exceed the equilibrium concentration due to nonuniformity of the gas concentration. In the MHD environment, to decompose  $\text{NO}_x$  to an environmentally acceptable level, a 2-s residence time has been suggested, a time that would allow sufficient time for the combustion gas equilibrium to occur. Despite some expected departures from equilibrium, the equilibrium model retains its value as a method for the prediction of the optimum conditions of operation.

Two methods may be considered for avoiding hot corrosion: (1) avoid the initial reaction between the liquid alkali sulfates and the protective metal oxide and (2) prevent the corrosive alkali sulfates from condensing in combustion systems. With respect to the first method, refractory oxides coatings have been considered and used; this subject has been reviewed in detail by Chatterji, Devries and Romeo.<sup>15</sup> With respect to the second method, the most powerful operational parameter is the control of the free oxygen concentration so that the combustion system is operated under slightly reducing conditions (see *e.g.*, Fig. 9). The condensation of  $\text{Na}_2\text{SO}_4$  as a liquid can be prevented by control of (a) the concentration of NaCl below 1 ppm (see, *e.g.*, Fig. 3) and/or (b) the concentration of HCl to 40 ppm or higher (see Fig. 4). Another parameter is the control of pressure. According to the results presented (Figs. 3-10) the higher the system pressure, the higher will be the  $\text{Na}_2\text{SO}_4$  condensation temperature. For optimum operation, a median system pressure such as 5 atm is suggested. Chemical additives can also be used. Harada<sup>16</sup> reported the effectiveness of injecting magnesium hydroxide into the fuel to prevent hot corrosion problems in heavy-oil-fired boilers. In the MHD environment, the  $\text{K}_2\text{CO}_3$  level should not exceed 100 ppm at temperatures below 1500 K to avoid the condensation of liquid  $\text{K}_2\text{SO}_4$  on the walls.

In principle, there is enough sulfur present in the combustion gas to convert all the alkalis into sulfates, or complex sulfates such as  $\text{K}_3\text{Fe}(\text{SO}_4)_3$  and  $\text{K}_3\text{Al}(\text{SO}_4)_3$ . However, in practice, this is not the case since sulfur maintains an equilibrium between  $\text{SO}_2$  and  $\text{SO}_3$  according to the reaction  $\text{SO}_3 \rightleftharpoons \text{SO}_2 + 1/2 \text{O}_2$ . The concentration ratios of  $\text{SO}_2$  and  $\text{SO}_3$  at various temperatures and pressures are shown in Fig. 11. At higher temperatures and lower pressures, the equilibrium is in favor of  $\text{SO}_2$ , whereas, at lower temperatures and higher pressures,  $\text{SO}_3$  is dominant. Figure 11 also shows that at the pressure close to that of conventional boilers, only a small amount of  $\text{SO}_3$  exists in the combustion gas, as has been observed.<sup>17</sup> Although  $\text{SO}_3$  was reported to be the species responsible for the formation of alkali complex sulfates and pyrosulfates, no such indication of the formation of  $\text{SO}_3$  was seen in this calculation. The percentages of sulfate conversion from NaCl,  $\text{K}_2\text{CO}_3$  and KCl are shown in Tables 2 and 3. With the addition of 100 ppm  $\text{K}_2\text{CO}_3$  to the combustion gas, 99% or more conversion to  $\text{K}_2\text{SO}_4$  took place at about 1005 K, which is 55 K higher than when no  $\text{K}_2\text{CO}_3$  was present. According to Table 3 at 1110 K,  $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$  are condensed largely as solid. The ideal binary solution model of the ANL-modified NASA CEC code<sup>12</sup> was used to examine the possibility of solutions between  $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$ . The result of the calculation indicates that the solid solution of both salts starts forming at temperatures of about 1174 K.

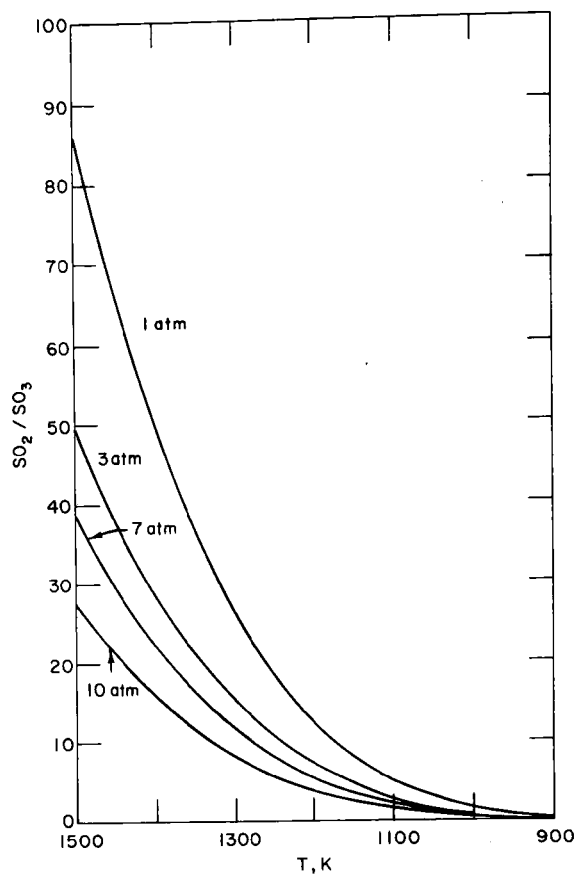


Fig. 11. Equilibrium Ratio of  $\text{SO}_2/\text{SO}_3$

Table 2. Percent Conversion of  $\text{NaCl}$  to  $\text{Na}_2\text{SO}_4$  and of  $\text{KCl}$  to  $\text{K}_2\text{SO}_4$  in a Typical Combustion Gas at 1 atm.

Conversion Product	Temperature, K					
	1500	1400	1300	1175	1050	950
$\text{Na}_2\text{SO}_4$ (g)	0.003	0.02	0.13	0.97	0.03	0
$\text{Na}_2\text{SO}_4$ (l)	0	0	0	30.08	0	0
$\text{Na}_2\text{SO}_4$ (s)	0	0	0	0	97.78	99.22
$\text{K}_2\text{SO}_4$ (s)	0	0	0	0	8.38	97.11

Table 3. Percent Conversion of NaCl to Na<sub>2</sub>SO<sub>4</sub>, and of K<sub>2</sub>CO<sub>3</sub> and KCl to K<sub>2</sub>SO<sub>4</sub> in a Typical Combustion Gas Doped with 100 ppm K<sub>2</sub>CO<sub>3</sub> at 1 atm.

Conversion Product	Temperature, K					
	1500	1410	1305	1200	1110	1005
K <sub>2</sub> SO <sub>4</sub> (g)	34.76	63.22	51.99	4.47	0.21	0.02
K <sub>2</sub> SO <sub>4</sub> (s)	0	0	26.41	83.85	97.23	99.85
Na <sub>2</sub> SO <sub>4</sub> (g)	0.46	2.82	7.10	1.72	0.16	0
Na <sub>2</sub> SO <sub>4</sub> (l)	0	0	0	18.28	0	0
Na <sub>2</sub> SO <sub>4</sub> (s)	0	0	0	0	82.18	99.25

## V. CONCLUSION

The equilibrium composition of the combustion gas and the condensation temperatures of sodium and potassium sulfates have been calculated as a function of the concentrations of NaCl, HCl, SO<sub>2</sub> and O<sub>2</sub>, and the system pressure. It was found that the order of the effectiveness of controlling the chemical activities of alkali sulfates is O<sub>2</sub> > HCl > NaCl > SO<sub>2</sub>. A system pressure of about 5 atm, concentrations of NaCl of less than 10 ppm, and concentrations of HCl of 40 ppm or higher are suggested as optimum operational conditions in the oxidizing environment. However, the use of a reducing environment is most effective. In the open-cycle MHD system, the level of K<sub>2</sub>CO<sub>3</sub> of 100 ppm or lower is considered to be the optimum concentration in the temperature range from 1500 to 900 K.

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